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Structural and dielectric properties of $KLiMoO_4$ ceramic

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Abstract : Potassium lithium molybdates ($KLiMoO_4$) ceramic has been prepared by solid state reaction technique. Preliminary structural study suggests the formation of single phase (monoclinic) compound at room temperature. The variation of dielectric constant and loss as a function of temperature (from room temperature to 250°C) at 1 kHz and 10 kHz exhibits dielectric anomaly and sequential phase transitions at T_{C1} = 134°C and T_{C2} = 48°C respectively. A comparison of various properties of $KLi(Mo_xW_{1-x})O_4$, x = 0 [*J. Mater. Sci. Lett.*, **16** 1807 (1997)], 0.5 [*J. Mater. Sci. Lett.*, **18** 501 (1999)] and 1.0 ceramics have also been made. The ferro-paraelectric phase transition (T_{C1}) has been found to be first order Curie-Weiss type.

Keywords : Phase transition, dielectric constant, structure.

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1. Introduction

Among the oxide ferroelectrics studied so far some rare earth, alkali ion and/or lead based molybdates and tungstates have been found to be attractive because of their wide variety of crystal structures and physical properties [1–15]. Some of them also exhibit a remarkable piezoelectric effect, ferroelastic effect and second harmonic generation [16]. It has been found that some molybdates and tungstates of the general formula $ACBO_4$ [A ≡ monovalent large cation; C ≡ small size cation; and B ≡ Mo and/or W], belonging to the cristobalite family [5,17,18], generally exhibit sequential phase transitions from the high temperature cubic phase (point group $\bar{4}3m$) to the low temperature ferroelectric disordered orthorhombic (point group $mm2$) and/or monoclinic (point group m) phase. The crystal structure of this family is mainly based on the framework of corner-sharing MoO_4 or WO_4 tetrahedra and the stability of the cubic phase is supported either by a disorder of the oxygen atom positions or dynamical vibration of the tetrahedral group as a whole [18,19].

Continuous attempts have been made to investigate $A^+LiB^{6+}O_4$ compounds, where A ≡ Na, K, Rb, Cs; B ≡ Mo and/or W, (*e.g.* $CsLiWO_4$, $CsLiMoO_4$, $RbLiWO_4$, $RbLiMoO_4$, $KLiWO_4$, $NaLiWO_4$ *etc.*) with desired characteristics from both theoretical and application points of view [5–15].

In order to check the existence of sequential phase transitions in $KLiMoO_4$ and for better understanding of these pseudo-proper ferroelectrics, preliminary structural and detailed dielectric studies of the compound was made. Besides a comparison of different observations have also been made between $KLi(Mo_xW_{1-x})O_4$; x = 0 [9], 0.5 [10] and 1.0 ceramics. The present paper about sequential phase transitions in $KLiMoO_4$ ceramic is a part of our systematic study on the $ACBO_4$ family [7–13].

2. Experimental

Polycrystalline $KLiMoO_4$ (abbreviated, hereafter, KLM) was prepared from high purity AR-grade K_2CO_3, Li_2CO_3 and MoO_3 by a high temperature solid state reaction technique. The detailed procedure adopted, for preparation are described elsewhere [7–12]. The calcination and sintering temperature was 500°C for 17 h and 520°C for 16 h respectively. The completion of the reaction and the formation of the desired compound were checked by X-ray diffraction.

For preliminary structural studies, the X-ray diffractogram of KLM, was recorded at room temperature using an X-ray diffractometer (Philips PW 1840) with

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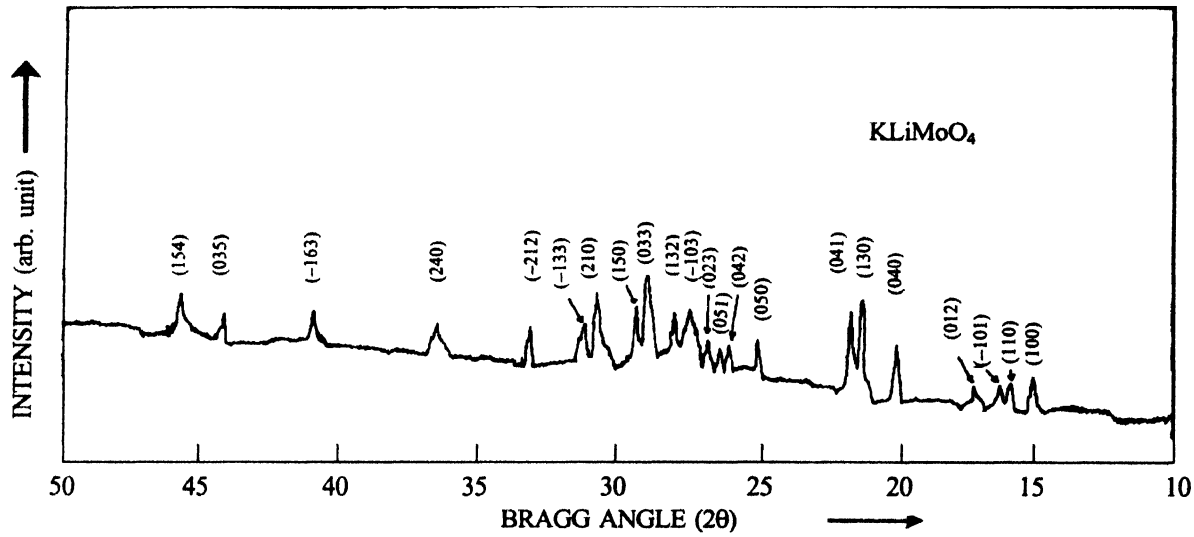

Figure 1. XRD pattern of $KLiMoO_4$ ceramic at room temperature.

monochromatized CuK∝ radiation (λ = 0.15418 nm) over a wide range of Bragg angles ($10° \leq 2\theta \leq 70°$) with a scanning speed of 2° min^{-1}. A sintered pellet was polished and electroded with air drying silver paste. The measurements of the dielectric constant (ε) and dielectric loss (tan δ) were carried out on a GR 1620AP capacitance measuring assembly, both as a function of frequency (400 Hz to 10 kHz at room temperature) and temperature (room temperature to 250°C at 1 and 10 kHz) using a three-terminal sample holder co-axially placed in a furnace built for this purpose. To overcome the effect of moisture, if any, on electrical properties the sample was pre-heated to 150°C and then cooled to room temperature prior to conducting the measurements.

3. Results and discussion

Figure 1 shows the X-ray diffraction pattern of $KLiMoO_4$ ceramic taken at room temperature. All reflection peaks of the X-ray profile were indexed, and the lattice parameters were determined using a least square refinement method with the help of a standard computer program (POWD). Good agreement between the observed and calculated inter-planer spacing (d-values) and there is no trace of any extra peaks, or peaks due to constituent oxides, suggest that the compound is having single phase monoclinic structure. The lattice parameters were found to be a = 5.948(6) Å, b = 17.903(7) Å, c = 10.954(3) Å and β = 96.853°. The average particle size estimated from some strong reflections [(040), (130), (041), (033) and (210)], of low 2θ values of the X-ray profile using Scherrer's equation [9,10] was found to be ~30 nm.

Figure 2 shows the variation of ε and tan δ with frequency at room temperature. Both ε and tan δ follow inverse dependence of frequency. This typical behaviour indicates that KLM behaves like a normal dielectric where different types of polarization mechanisms might be present. We find a similar dielectric behaviour with respect to frequency in other samples of this family *viz.* $KLiWO_4$ [9] and $KLiMo_{½}W_{½}O_4$ [10].

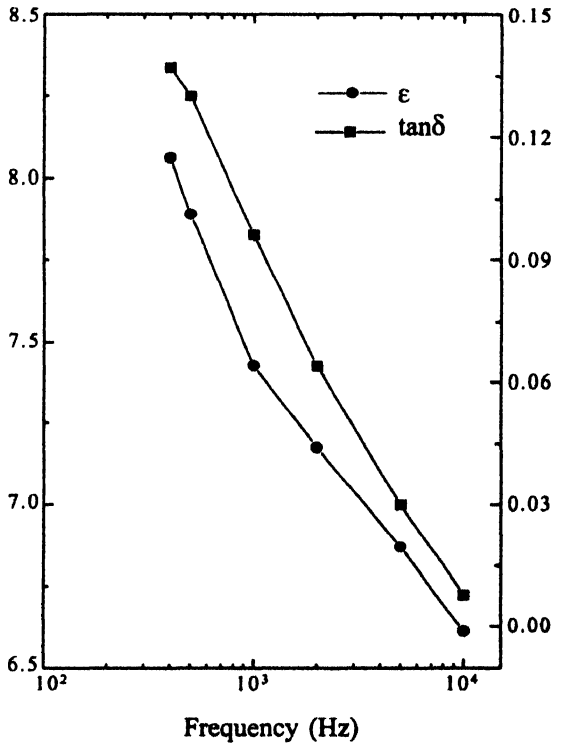

Figure 2. Variation of ε and tan δ with frequency of $KLiMoO_4$ ceramic at room temperature.

The temperature dependence of the relative permittivity (ε) and loss (tan δ) of KLM at 1 kHz and 10 kHz shows successive phase transitions (Figure 3). The successive

phase transitions might be of the type: ferroelastic-ferroelectric (transition temperature T_{C2} = 48°C) and ferroelectric-paraelectric (transition temperature T_{C1} = 134°C) [1,4,14-17]. The value of ε_{max} at T_{C1} and T_{C2} at 1 kHz is found to be 26.02 and 7.89 respectively. We find the value of ε_{max} decreases with increasing frequency (Figure 3). The difference between the values of ε_{max} (T_{C1}) measured at 1 kHz and 10 kHz is found to be 14.35 and the difference at ε_{max} (T_{C2}) is 0.82.

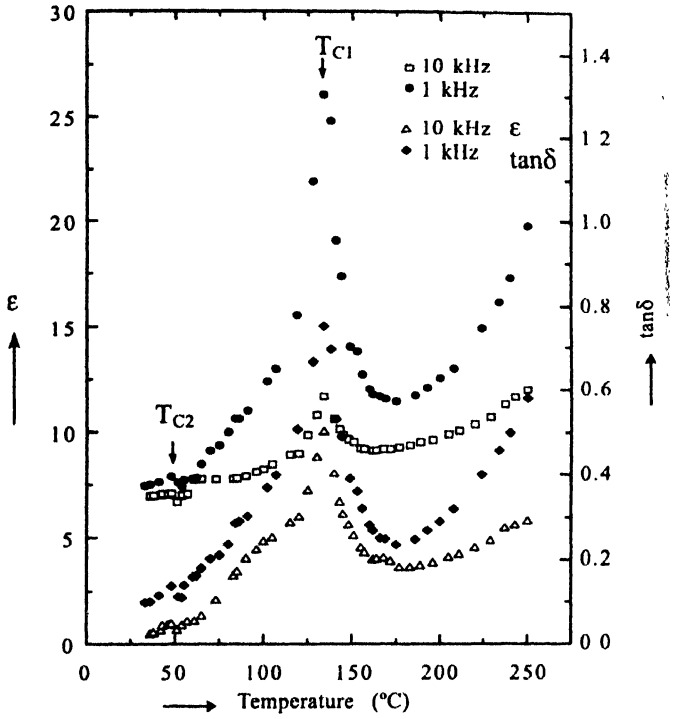

Figure 3. Variation of ε and tan δ with temperature of $KLiMoO_4$ ceramic at 1 kHz and 10 kHz.

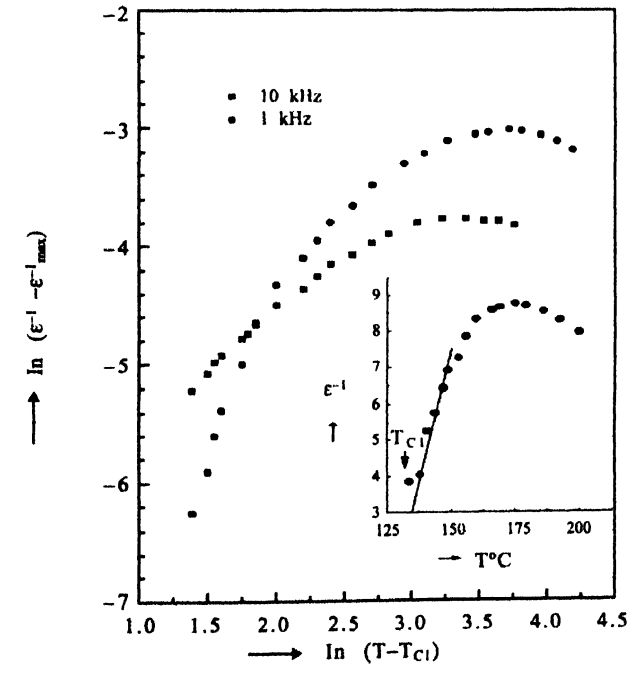

Figure 4. Variation of $\ln(1/\varepsilon - 1/\varepsilon_{max})$ with $\ln(T - T_{C1})$ of $KLiMoO_4$ ceramic at 1 kHz and 10 kHz.

To examine the diffusive character of the ferro-paraelectric phase transition (T_{C1}), we have plotted ($1/\varepsilon - 1/\varepsilon_{max}$) *versus* ($T - T_{C1}$) in a logarithmic representation (Figure 4). The graph does not show a linear behaviour but a continuous change in the slope as the temperature changes. Thus, it was difficult to determine the value of n (varies between 1 – normal Curie-Weiss type and 2-typical diffuse transition type), the exponent in the expression : $1/\varepsilon - 1/\varepsilon_{max} = A(T-T_{max})^n$, which represents the diffusivity of the transition. Therefore, the value of n was estimated by the method of least squares. The details of the fitting procedure adopted, is described elsewhere [20]. The value of n was found to be 1.16. Value of $n \approx 1$, the shift in peak temperature, $\Delta T_{max} = T_{max}(10\text{ kHz}) - T_{max}(1\text{ kHz}) = 0$ and T_{C1} as obtained from ε and tan δ measurements coincide, suggests that ferro-paraelectric phase transition is of Curie-Weiss type. The reciprocal of the dielectric constant (ε^{-1}) varies almost linearly with the temperature, T above T_{C1}, in the paraelectric phase (Figure 4, inset) and obeys the Curie-Weiss law : $\varepsilon = C/(T-T_0)$, where C and T_0 are the Curie-Weiss constant and Curie-Weiss temperature respectively. It is also clear from the inset of Figure 4 that $T_{C1} \approx T_0$ (132°C) which implies the phase transition to be of the first order. In order to check these transition temperatures repeated dielectric measurements were made after a gap of six months. The variation in ε was found to be within 2–3% at temperatures higher than 80°C only, however the dielectric anomaly was observed at the same T_C's.

An estimation of the activation energies E_{af} and E_{ap}, in the ferroelectric and paraelectric phases from the variation of $\ln\sigma$ with $10^3/T$ at 1 kHz (Figure 5), using the relation $\sigma = \sigma_0 \exp[-E_a/k_BT]$ where σ_0 is a constant and k_B is Boltzmann constant have also been made and were found as 0.41 eV and 1.09 eV respectively. The values of these energies are found to be small compared to other ferroelectric oxides. This may possibly be due to low dielectric constant of the compound. A change in slope corresponding to T_{C1} was also observed in $\ln\sigma - 10^3/T$ dependence (Figure 5). This is the indicative of structural change near the phase transition and is accompanied by a change in the activation energy of carriers [14,21].

Figure 6 shows the variation of the transition temperatures (T_{C1} and T_{C2}), unit cell volume, ε_{RT} and tan δ_{RT} with molybdenum content (x) in $KLi(Mo_xW_{1-x})O_4$; x = 0, 0.5 and 1.0 ceramics. It is evident from this figure that T_{C1}, T_{C2} and the unit cell volume decreases with the increase in molybdenum content (x). However, the value of ε_{RT} and tanδ_{RT} is maximum at x = 0.5 *i.e.* for $KLiMo_{0.5}W_{0.5}O_4$. This may happen probably due to increasing disorder in the system. The above system undergoes to lowest symmetry (triclinic structure) [10] while KLM and KLW [9] have a monoclinic structure. We also find a similar trend for ε_{max} and tan δ_{max}. It is to be further noted that for x = 0.5 composition, the calcination temperature has reduced drastically to 350°C [10] as compared to 500°C for x = 0 *i.e.* $KLiWO_4$ [9] and x = 1 *i.e.* $KLiMoO_4$ the present ceramic.

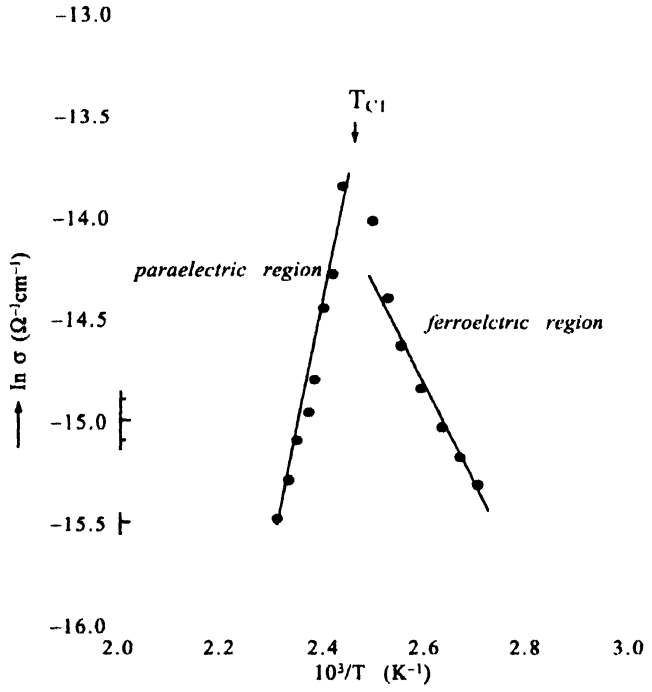

Figure 5. Variation of ln σ with $10^3/T$ of $KLiMoO_4$ ceramic at 1 kHz.

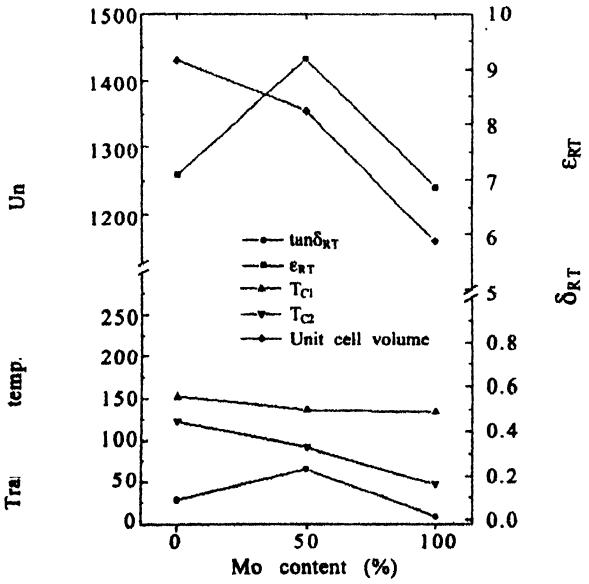

Figure 6. Variation of transition temperature, unit cell volume, room temperature value of ε and tan δ with molybdenum content (%) in $KLi(Mo_xW_{1-x})O_4$; x = 0, 0.5 and 1.0 ceramics.

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